NIST assessment of ITS-90 non-uniqueness for 25.5 ohm SPRTs at gallium, indium, and cadmium fixed points

G. F. Strouse

National Institute of Standards and Technology
Process Measurements Division
Gaithersburg, MD 20899

ABSTRACT

The use of temperature subranges in the definition of the International Temperature Scale of 1990 (ITS-90) permits standard platinum resistance thermometers (SPRTs) to be measured at defining fixed points of a particular subrange as well as at fixed points not utilized in that subrange. These redundant fixed points allow analysis of the non-uniqueness of the scale. Specifically, with 25.5 ohm SPRTs at gallium, indium, and cadmium fixed points have been made and examined to determine the non-uniqueness at these points. The results of this investigation indicate that the levels of non-uniqueness of the ITS-90 at the three redundant fixed points does not contribute significantly to the total error associated with the calibration of an SPRT.

SUBJECT INDEX: International Temperature Scale of 1990 (ITS-90), Platinum resistance thermometers and Thermometry, Fixed points

INTRODUCTION

Different thermometers indicate slightly different apparent temperatures at any given point between the defining fixed-point temperatures used in the calibration of those thermometers. These deviations are known as the scale non-uniqueness. The International Temperature Scale of 1990 (ITS-90) (1) allows a standard platinum resistance thermometer (SPRT) to be calibrated over multiple temperature subranges. Specified thermometric fixed points are used to define the ITS-90 and for the calibration of SPRTs over any one of these subranges. Thermometers may also be measured at "redundant" fixed points, i.e, those not used in the calibration of SPRTs for that particular subrange of the ITS-90. Measurements of SPRTs at such redundant fixed points allow for an estimate of the non-uniqueness of the ITS-90 at those temperatures.

The results of an investigation of the ITS-90 non-uniqueness for 25.5 ohm SPRTs at the gallium triple point (302.9166 K) and the indium (429.7485 K) and cadmium (594.219 K) (2) freezing points are presented.

The observed non-uniqueness in the ITS-90 is inherent in the mathematics and in the small variations in the construction of each SPRT. Interpolation of temperature between the defining temperature subrange fixed points yields, at each point, a different apparent temperature for each SPRT. The mathematical functions and scale criteria are designed to minimize the non-uniqueness that is observed with SPRTs. The addition of multiple subranges has increased the flexibility in the SPRT usage for defining the temperature scale. However, this increased flexibility exacerbates the uncertainty as to which temperature subrange should be used for the calibration of an SPRT. The present investigation of all possible subranges eventually will help to determine whether there is a systematic difference in the levels of non-uniqueness of these subranges.

EXPERIMENTAL DETAILS

The National Institute of Standards and Technology (NIST) maintains all of the defining fixed points of the ITS-90 over the range 83.8058 K to 1234.93 K, as well as the freezing point of cadmium. Using these fixed points, the staff of the Platinum Resistance Thermometry (PRT) Laboratory at NIST calibrates 25.5 Ω SPRTs as the defining interpolation standard for the realization of the ITS-90 from the argon triple point (83.8058 K) to either the zinc (692.677 K) or aluminum (933.473 K) freezing point. The subranges from 273.15 K up to and including the Al freezing point were used in the determination of the scale non-uniqueness presented in this paper. Table I provides a list of the temperature subranges, the subrange defining fixed points required for SPRT calibrations, the redundant fixed points within each subrange, and the number of SPRTs used at each redundant fixed point for each temperature subrange involved in this investigation.

The redundant fixed-point temperatures involved in this study (cadmium, indium and gallium) lie within several temperature subranges. The realized temperatures of the redundant fixed points, as with all fixed points, must be corrected for hydrostatic head and pressure effects relative to their assigned value. All resistance measurements reported here reflect zero-power dissipation to remove any error associated with self-heating effects. Zero-power values were calculated by making measurements at 1 mA and 2 mA, and extrapolating to 0 mA.

Table I: Subranges, defining fixed points and redundant fixed points. TPW refers to the triple point of water.

Temperature Subrange	Calibration fixed points	Redundant fixed points	Number of SPRTs
273.15 K to 429.7485 K	In, TPW	Ga	59
273.15 K to 505.078 K	Sn, In, TPW	Ga	50
273.15 K to 692.677 K	Zn, Sn, TPW	Ga, In, Cd	62, 45, 157
273.15 K to 933.473 K	Al, Zn, Sn, TPW	Ga, In, Cd	14, 14, 37

As shown in Table I, a large number of SPRTs were calibrated at NIST over the four temperature subranges that were used in the calculation of non-uniqueness at the three redundant fixed points. A cross sampling of thermometers was included to investigate whether different models yielded systematically different results. Table II shows a descriptive list of the manufacturers, the SPRT models and the number of each model used in the study.

Table II: List of manufacturers, models and number of each type of SPRT used for the calculation of non-uniqueness.

	Number of SPRTs for the redundant fixed points Cd, In, Ga of the four subranges			
Manufacturer/Model*	273.15 K to Al	273.15 K to Zn	273.15 K to Sn	273.15 K to In
Chino R800-2	4, 1, 1	4, 1, 1	-, -, 1	-, -, 1
L&N 8163	6, 1, 2	62, 19, 25	-, -, 21	-, -, 25
L&N 8167	2, 0, 0	16, 4, 5	-, -, 4	-, -, 4
Rosemount 162C	0, 0, 0	6, 2, 2	-, -, 2	-, -, 2
Rosemount 162CE	24, 12, 10	40, 14, 20	-, -, 16	-, -, 21
YSI 8163	0, 0, 1	17, 3, 4	-, -, 3	-, -, 3
YSI 8167	1, 0, 0	12, 2, 5	-, -, 3	-, -, 3

The SPRTs of this investigation were calibrated on the ITS-90 using the following standard NIST procedures (3). First, the thermometers were annealed at a temperature higher than that of their hottest fixed-point measurement. Special thermal treatment was given to those SPRTs requiring calibration up to the aluminum freezing point. Second, the thermometers were measured at the triple point of water (TPW) (273.16 K) to establish a baseline for their stability during the entire calibration cycle.

Third, the SPRT was sequentially measured at the fixed points, decreasing in hotness, and bracketed by measurements at the TPW. A typical example of a measurement sequence for a thermometer is: anneal, TPW, Al, TPW, Zn, TPW, Cd, TPW, Sn (505.078 K), TPW, In, TPW, Ga, TPW, Hg (234.3156 K), TPW, Ar and TPW. The measurements were performed using a semi-automated, computer-controlled data-acquisition system. The automatic 30 Hz ac resistance bridge, ac/dc reference resistors, digital multimeter, thermometer port connections and scanners are all connected via IEEE-488 connections. The data acquisition program allows the computer to accept measurement data only when the thermometer is at thermal equilibrium. The total change in the resistance of the SPRT at the TPW must not exceed the equivalent of 0.75 mK for glass-sheathed, and 1.0 mK for metal-sheathed, thermometers. Also, the SPRT must meet the ITS-90 criterion of $W(\mathrm{Ga}) \geq 1.118\,07$ or $W(\mathrm{Hg}) \leq 0.844\,235$ $[W(T_{90}) = (R(T_{90})/(R(273.16\ \mathrm{K})]$. A calibration included from one to three of the redundant fixed points.

The non-uniqueness at the gallium triple point was determined for four temperature subranges including: 273.15 K to 429.7485 K, 273.15 K to 505.078 K, 273.15 K to 692.677 K, and 273.15 K to 933.473. At NIST, the gallium point is realized as a triple point instead of the ITS-90 assigned melting point. The purity of the metal used in the construction of this Ga fixed point cell was 99.99999%. The estimated total (random+systematic) uncertainty (1 σ) in the NIST realization of the triple-point temperature of this cell is ± 0.1 mK (3). The random uncertainty of W(Ga) values obtained for the gallium check thermometer over 20 months is ± 0.03 mK (3).

The non-uniqueness at the freezing point of indium was determined with two different subranges: 273.15 K to 692.677 K and 273.15 K to 933.473 K. The purity of the In sample is 99.9999^{+}%. The estimated total uncertainty (1 σ) for the NIST indium freezing point is ± 0.7 mK (3). Measurements of W(In) values with the indium check thermometer over a 20 month time period yielded a random uncertainty of ± 0.14 mK (3).

The cadmium freezing point is not a defining fixed point of the ITS-90. It is used at NIST as a secondary reference point (a check point) in the calibration of SPRTs. The purity of cadmium metal used in the construction of the fixed-point cell was 99.9999%. The freezing-point temperature of this cell (594.219 K) was determined from measurements with 18 NIST SPRTs using all possible fixed points from 273.15 K to 933.473 K (2). This temperature was calculated from the average of the measured W(Cd) values, using the calibration coefficients and deviation functions of all possible temperature subranges. The estimated total uncertainty (1 σ) of the NIST freezing point of cadmium is ± 1.0 mK (3). Twenty months of W(Cd) values for the check SPRT used to monitor the cadmium freezing point had a random uncertainty of ± 0.22 mK (3). The non-uniqueness at this point was determined by using two subranges: 273.15 K to 692.677 K and 273.15 K to 933.473 K.

Table III: Calibration uncertainties (1 σ) for each temperature subrange at each redundant fixed point.

Temperature Subrange	Random calibration uncertainties, mK		
	Cd	In	Ga
273.15 K to 492.7485 K	-------	-------	0.03
273.15 K to 505.078 K	-------	-------	0.21
273.15 K to 692.677 K	0.33	0.36	0.11
273.15 K to 933.473 K	0 33	0.45	0.19
Random uncertainty of fixed point	0.22	0.14	0.03

In addition to the uncertainties associated with each redundant fixed point, there are random uncertainties associated with each defining fixed point for a given temperature subrange. The systematic uncertainties are not to be included since all thermometers are calibrated with the same measurement system and the same thermometric fixed points. Also, there is no systematic uncertainty for the redundant fixed points because they are not being measured for the determination of their temperature, but are being used as constant temperature environment. The error propagation of the random uncertainties from the defining fixed points gives the uncertainty at each of the redundant fixed points for each possible temperature subrange. The error propagated from each defining fixed point is calculated for each subrange by assuming the error of that fixed point with no error at the other fixed points, and determining mathematically how that error propagates throughout the entire subrange. The estimated random uncertainty for each of the temperature subranges at the redundant fixed-point temperatures was calculated using the root sum square (RSS) error from the propagated random errors of the defining fixed points (3). Table III lists this RSS error at each redundant fixed-point temperature for each subrange and also the random uncertainty for each redundant fixed point.

RESULTS

The non-uniqueness at each of the redundant fixed points was calculated for each of the given temperature subranges using measurements on all relevant SPRTs. For each temperature subrange, the relevant coefficients for the appropriate deviation function for each SPRT were used in the calculations. Table IV provides a summary of the non-uniqueness values obtained from this investigation. In Figures 1, 2, 3 and 4 the different symbols in the plots represent the different subranges and different manufacturer/models. The symbol key for the figures for the manufacturer/models are as follows: A) solid and open squares, B) solid and open diamonds, C) solid and open triangles, D) short dash and star, E) solid and open circles, F) long dash and shaded square and G) plus and x. The keyed symbols for each manufacturer/model represent the same thermometer for the different subranges, when they are in the same position along the abscissa. Not all of the manufacturer/models are represented in every temperature subrange, since it is not advisable to heat SPRTs with mica supports up to 933.473 K. Table II shows which manufacturer/models were used to determine the non-uniqueness for the redundant fixed points for the various temperature subranges.

Table IV: Summary of ITS-90 non-uniqueness values.

Temperature Subrange	Non-uniqueness, ±mK		
	Cd	In	Ga
273.15 K to 492.7485 K	-------	-------	0.17
273.15 K to 505.078 K	-------	-------	0.16
273.15 K to 692.677 K	0.45	0.28	0.13
273.15 K to 933.473 K	0.43	0.22	0.12
Estimated total	0.45	0.28	0.17

Gallium triple point

For each of the temperature subranges, the calculated non-uniqueness for the gallium triple point, was as follows: 1) ± 0.17 mK for 273.15 K to the In freezing point, 2) ± 0.16 mK for 273.15 K to the Sn freezing point, 3) ± 0.13 mK for 273.15 K to the Zn freezing point, and 4) ± 0.12 mK for 273.15 K to the Al freezing point. The non-uniqueness at the gallium triple point for all of the measured 25.5 Ω SPRTs is about ± 0.17 mK. Figure 1 shows the non-uniqueness at the gallium triple point for the subranges 273.15 K to 933.473 K and 273.15 K to 692.677 K. Figure 2 shows the non-uniqueness at the gallium triple point for the subranges 273.15 K to 505.078 K and 273.15 K to 429.7485 K.

To check for systematic differences or a difference between the assigned ITS-90 temperature and the NIST fixed-point-cell temperature, the mean (M) of the non-uniqueness values was calculated. The mean values of non-uniqueness for each temperature subrange are as follows: 1) -0.01 mK for 273.15 K to the In freezing point, 2) 0.01 mK for 273.15 K to the Sn freezing point, 3) 0.05 mK for 273.15 K to the Zn freezing point and 4) 0.04 mK for 273.15 K to the Al freezing point. The overall mean of the non-uniqueness is about 0.02 mK.

Analysis of variance (ANOVA) is a procedure for comparing multiple populations, "F" is the F statistic, "MSE" is the mean square error and "p" is the probability level (4). ANOVA makes only one comparison to determine if any of the populations differ from the rest. In the case of a significant ANOVA, post-hoc comparison tests (e.g. Scheffé) evaluating individual population means are performed to determine the actual source of differences (4).

The results of a 7 (manufacturer/model) X 4 (temperature subrange) ANOVA yielded the following results. First, there was a significant main effect for manufacturer/model ($F(6,160)=6.28$, $MSE=0.004$, $p \leq 0.0001$). Post-hoc Scheffé tests revealed that two of the manufacturer/models had a significantly higher non-uniqueness than two other manufacturer/models. However, these differences are within the uncertainty of the measurements.

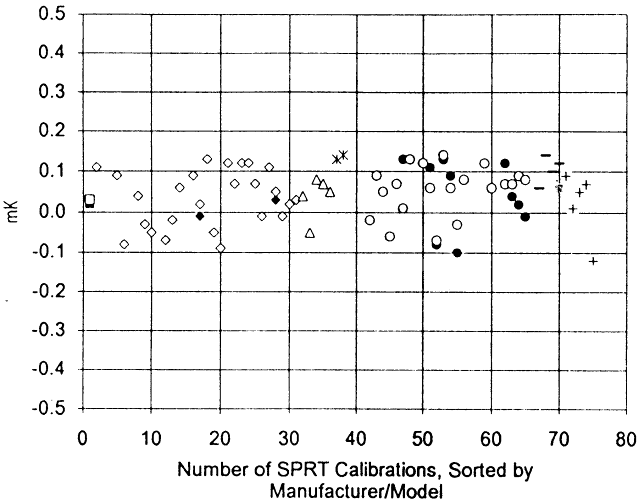

Figure 1. Non-uniqueness at the triple point of gallium for the subranges 273.15 K to 692.677 K (Zn) and 273.15 K to 933.473 K (Al). The solid symbols and the shaded square are for the subrange 273.15 K to Al and the open symbols, plus, long dash and star are for the subrange 273.15 K to Zn. The 273.15 K to Zn subrange has seven different manufacturer/models and the 273.15 K to Al subrange has four different manufacture/models represented. The symbol key for the manufacturer/models are as follows: A) solid and open squares, B) solid and open diamonds, C) open triangles, D) star, E) solid and open circles, F) long dash and shaded square and, G) plus. The keyed symbols for each manufacturer/model represent the same thermometer for the different subranges, when they are in the same position along the abscissa.

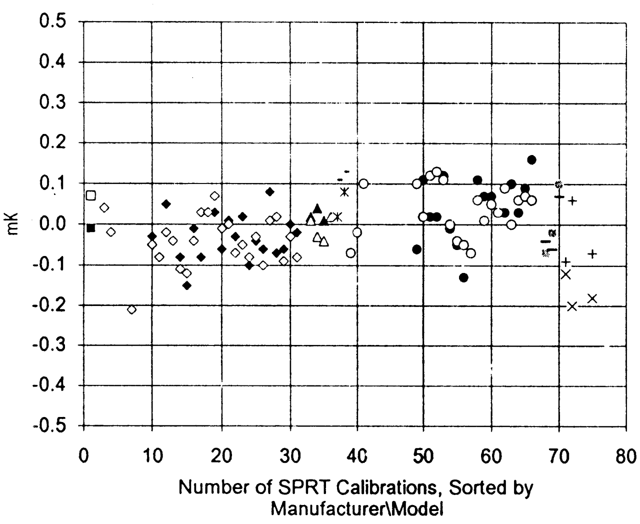

Figure 2. Non-uniqueness at the triple point of gallium for the subranges 273.15 K to 429.7485 K (In) and 273.15 K to 933.473 K (Sn). The solid symbols, shaded square, short dash and plus are for the subrange 273.15 K to Sn and the open symbols, long dash, star and x are for the subrange 273.15 K to In. The 273.15 K to In subrange has seven different manufacturer/models and the 273.15 K to Sn subrange has seven different manufacture/models represented. The symbol key for the manufacturer/models are as follows: A) solid and open squares, B) solid and open diamonds, C) solid and open triangles, D) short dash and star, E) solid and open circles, F) long dash and shaded square and, G) plus and x. The keyed symbols for each manufacturer/model represent the same thermometer for the different subranges, when they are in the same position along the abscissa.

Second, there was a significant main effect for temperature subrange ($F(3,160)=4.22$, $MSE=0.004$, $p\leq0.01$). Post-hoc Scheffé tests yielded a significant difference in non-uniqueness between the 273.15 K to Zn ($M=0.05$) and the 273.15 K to Sn ($M=0.01$) subranges and the 273.15 K to Zn ($M=0.05$) and the 273.15 K to In ($M=-0.01$) subranges respectively. These systematic differences, however, are within the random uncertainty of the gallium triple point plus the random uncertainty from the error propagated from the defining fixed points of the appropriate subranges.

Indium freezing point

The non-uniqueness at the indium freezing point is ±0.28 mK for the temperature subrange 273.15 K to the Zn freezing point and ±0.22 mK for 273.15 K to the Al freezing point. The estimated non-uniqueness at the indium freezing point for all of the measured SPRTs is about ±0.28 mK. Figure 3 shows the non-uniqueness at the freezing point of indium for each possible temperature subrange. The data do not show any apparent systematic differences between the different temperature subranges or the different manufacturer/models. This was confirmed by the lack of significant effects from a 7 (manufacturer/model) X 2 (temperature subrange) ANOVA. There is, however, a systematic temperature difference between the calculated $W(\mathrm{In})$ and the measured $W(\mathrm{In})$ values. The mean values of non-uniqueness for each temperature subrange are 0.18 mK for 273.15 K to Zn and 0.10 mK for 273.15 K to Al. The overall mean of the non-uniqueness is about 0.14 mK. It must be noted, however, that this systematic difference is within the uncertainty placed on the indium freezing point plus the error propagated by the defining fixed points.

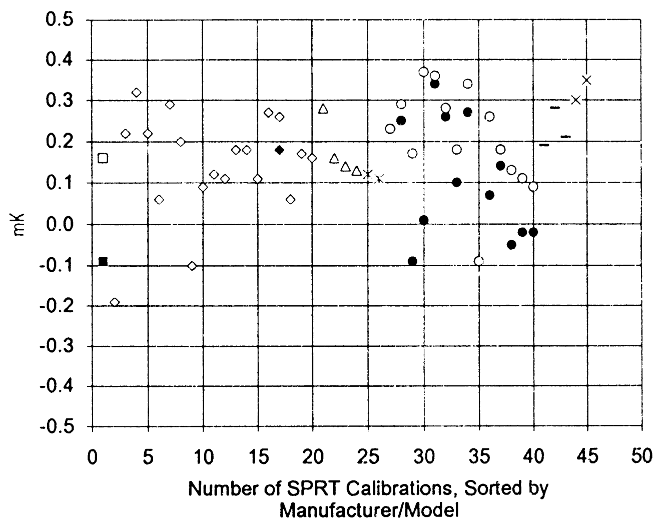

Figure 3. Non-uniqueness at the freezing point of indium for the subranges 273.15 K to 692.677 K (Zn) and 273.15 K to 933.473 K (Al). The solid symbols are for the subrange 273.15 K to Al and the open symbols, x, long dash, and star are for the subrange 273.15 K to Zn. The 273.15 K to Zn subrange has seven different manufacturer/models and the 273.15 K to Al subrange has three different manufacture/models represented. The symbol key for the manufacturer/models are as follows: A) solid and open squares, B) solid and open diamonds, C) open triangles, D) star, E) solid and open circles, F) long dash and, G) x. The keyed symbols for each manufacturer/model represent the same thermometer for the different subranges, when they are in the same position along the abscissa.

Cadmium freezing point

The non-uniqueness at the cadmium freezing point is ±0.45 mK for the subrange 273.15 K to the Zn freezing point and ±0.43 mK for the subrange 273.15 K to the Al freezing point. The estimated non-uniqueness at the cadmium freezing point, based on the results of all of the measured SPRTS for all of the temperature subranges, is about ±0.45 mK. Figure 4 shows the non-uniqueness associated with measurements made at the cadmium freezing point. The mean values of non-uniqueness for each temperature subrange are -0.00(5) mK for 273.15 K to Zn and -0.02 mK for 273.15 K to Al. The overall mean of the non-uniqueness is about -0.01 mK which shows close agreement with value assigned to the NIST Cd fixed-point cell.

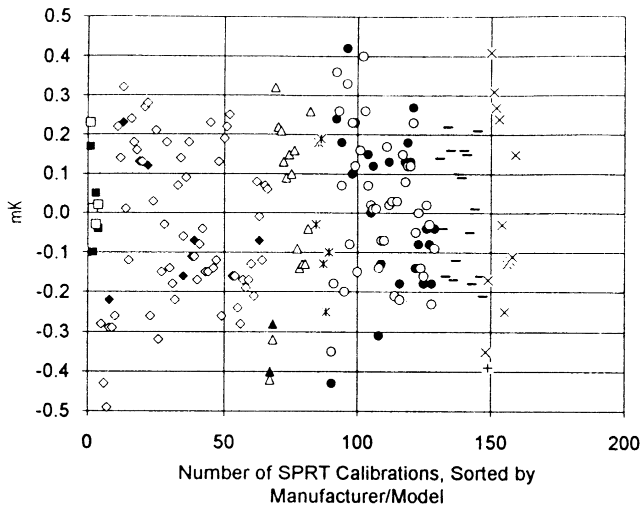

Figure 4. Non-uniqueness at the freezing point of cadmium for the subranges 273.15 K to 692.677 K (Zn) and 273.15 K to 933.473 K (Al). The solid symbols and the plus are for the subrange 273.15 K to Al and the open symbols, x, long dash, and star are for the subrange 273.15 K to Zn. The 273.15 K to Zn subrange has seven different manufacturer/models and the 273.15 K to Al subrange has five different manufacture/models represented. The symbol key for the manufacturer/models are as follows: A) solid and open squares, B) solid and open diamonds, C) solid and open triangles, D) star, E) solid and open circles, F) long dash and, G) plus and x. The keyed symbols for each manufacturer/model represent the same thermometer for the different subranges, when they are in the same position along the abscissa.

A 7 (manufacturer/model) X 2 (temperature subrange) ANOVA yielded only a significant temperature subrange main effect ($F(1,182)=7.31$, $MSE=0.037$, $p\leq0.01$). The 273.15 K to Al subrange ($M=-0.02$) evidenced a larger mean value of non-uniqueness than the 273.15 K to Zn subrange ($M=-0.00(5)$). This systematic difference is within the random uncertainty placed on the cadmium freezing point plus the error propagated from the defining fixed points for the appropriate subranges. The lack of an apparent systematic difference in the non-uniqueness between manufacturer/models was confirmed by the non-significant ANOVA manufacturer/model main effect.

CONCLUSIONS

The non-uniqueness of the set of SPRTs used in this investigation did not show any significant differences between temperature subranges or manufacturer/models. While the statistical tests, however, show some systematic differences, those differences are within the random uncertainties of the SPRT calibrations. The mean of the non-uniqueness values determined are effectively zero except for that at the indium freezing point where there is an apparent systematic offset of the temperature value of the NIST cell from that assigned (ITS-90) to the freezing point of indium.

The values of non-uniqueness are within the random uncertainty of measurements based on the random uncertainties of the redundant fixed points plus the error propagated from the defining fixed points. Consequently, the non-uniqueness of the ITS-90 at the three redundant fixed points do not contribute significantly to the total error associated with the calibration of an SPRT.

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REFERENCES

* Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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